



Towards the complete dechlorination of chloroacetic acids in water by sonoelectrochemical methods: Effect of the cathode material on the degradation of trichloroacetic acid and its degradation by-products



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ABSTRACT

The effect that the cathode material has on the electrochemical and high-frequency sonoelectrochemical degradation of TCAA in water samples with no background electrolyte has been studied in the work here presented. For all the cathode materials employed (Ti, AISI 304 stainless steel, carbon and Pb), the high-frequency sonoelectrochemical treatment yielded significantly higher fractional conversions for trichloroacetic acid and a significantly higher degradation efficiency when considering the removal of chlorinated species from the treated solutions. Moreover, differences in fractional conversion, degradation efficiency, current efficiency, C mass balance error and the concentration of the different trichloroacetic acid degradation by-products show how the cathode material has a strong effect on the efficiency of the electrochemical and high-frequency sonoelectrochemical treatments and the degradation mechanisms that may take place. Regarding this, complete dechlorination was virtually achieved in the high-frequency sonoelectrochemical degradation using a Pb cathode, where C mass balance results suggested the mineralization of TCAA.

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1. Introduction

Chloroacetic acids (CAAs) are receiving an increasing attention from researchers and legislators around the world as they are becoming one of the largest fractions of disinfection by-products (DBPs) found in drinking waters [1–3], trichloroacetic acid (TCAA) being one of the most targeted CAAs in academic studies due to its widespread presence in the environment [4]. TCAA, a former herbicide, is not only one of the most common DBPs, but it is also formed by different natural processes [5–7] and is a common by-product of the degradation of other chlorinated organocompounds such as perchloroethylene [8,9]. The concentration of TCAA may lie within a wide range in surface and ground waters due to its high solubility and different natural and anthropological sources [4], and the increasing presence of TCAA and other CAAs (dichloroacetic acid

or DCAA and monochloroacetic acid or MCAA) in waters and soils constitutes a serious risk to human health [10,11]. In some cases, the exposure to TCAA and other CAAs is extremely high, as recently reported by Cardador and Gallego [12] who studied the exposure of workers and swimmers to TCAA, DCAA and MCAA in indoor and outdoor pools, finding that, in such places, TCAA and DCAA may reach concentration levels above the maximum concentration level set by the U.S. EPA [13] for haloacetic acids (HAAs). Traditional bioremediation methods have unsuccessfully been employed in the degradation of HAAs, including CAAs, in water, TCAA being the most recalcitrant among them [14,15]. Phase-transfer techniques such as adsorption have shown promising results [16] in recent years, although a more environmentally friendly approach where the degradation of the C–Cl bond, which is toxic in nature, is preferred.

In recent years, different chemical methods have been developed in order to degrade the C–Cl bond in CAAs, in general, and TCAA, in particular. Zero-valent iron and bimetallic particles [17–19] have been successfully used to remove TCAA and its degradation by-products. Nevertheless, the potential release of metals in these processes may affect water quality in long term [20] and

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therefore have a harmful effect on the environment [21]. Fe (II) minerals from corroded iron/steel pipes have also been employed with different results: while TCAA was not affected at all in the presence of goethite/magnetite and aqueous Fe (II) [22], TCAA and DCAA were removed in aqueous solutions containing a carbonate green rust [23]; however, no degradation of MCAA was noticed in the latter. Photocatalytic degradation over bare and silver-deposited TiO_2 was not very effective in removing TCAA from aqueous solutions [24], although it showed promising results in the degradation of DCAA and MCAA. And the catalytic hydrodechlorination over Pd/ZrO₂ catalysts has also been very effective in the degradation of TCAA, DCAA and MCAA in water [25]. Nevertheless, the small size of the Pd catalysts (from 1 to 3.5 nm) and the concentration used (150 mg/L) could potentially become an important issue in the scaling-up of the process.

The electrochemical degradation of CAAs in aqueous solutions has received a wide attention in the last years since Korshin and Jensen [26] studied the electroreduction of diverse HAAs on gold or copper electrodes, showing that both TCAA and DCAA were electrochemically active and could be reduced by electrochemical methods, although no signs of the degradation of MCAA were clearly observed in their study. Li et al. [27,28] showed that the dechlorination of HAAs on haemoglobin-loaded carbon nanotube (Hb/CNT) cathodes was stepwise, following in the case of TCAA the pathway of $\text{TCAA} \rightarrow \text{DCAA} \rightarrow \text{MCAA}$. However, very slow degradation rates were noticed for MCAA. This issue was resolved by Li et al. [29] with newly developed electrodes consisting of Pd/Fe nanoparticles electrodeposited onto carbon paper (Pd/Fe-C), achieving very high degradation rates for TCAA, DCAA and MCAA. All these results demonstrate that the electrochemical treatment of waters polluted with CAAs is technically feasible, although some important drawbacks arise from these studies that should be dealt with: (i) the use of expensive and/or rare cathodic materials that may not be commercially available (gold [26], Hb/CNT [27,28], Pd/Fe-C [29]), and (ii) the necessary addition of a background electrolyte (0.01 M Na_2SO_4 or 0.01 M K_2HPO_4 [26], 0.1 M phosphate buffer containing 10 mM KCl [27,28], 10 mM Na_2SO_4 [29]) in order to achieve a certain conductivity to prevent resistance-controlled kinetics and enable a good control of the electrochemical system.

The use of ultrasound in electrochemistry, also known as sono-electrochemistry, has been deeply studied and evaluated in recent years due to its potential application in environmental remediation [30]. In this sense, many research groups have demonstrated how ultrasound may catalyse the overall electrochemical degradation process of different chlorinated organocompounds such as diuron [31] or perchloroethylene [32], achieving for the latter the complete degradation of C-Cl bonds in water samples where no background electrolyte was added [33]. In previous studies by the authors, the removal of TCAA and its main degradation by-products, DCAA and MCAA, was also achieved by sonoelectrochemical methods [34,35], showing that high-frequency ultrasound and the absence of a background electrolyte were key parameters in order to achieve the complete dechlorination of TCAA. The use of high-frequency ultrasound did not only catalyse the progressive C-Cl bond cleavage mechanism, but also seem to enhance the dissociative adsorption/incineration paths that may occur on both cathode and anode. In addition, it was shown how the anode material may also affect the overall process, as complete dechlorination of TCAA was achieved when using a steel cathode and a PbO_2 anode.

The present work completes the study of the feasibility of high-frequency sonoelectrochemical methods as a way to completely remove CAAs in water by evaluating the effect that the cathode material may have on the process. The cathode material is expected to have a strong influence on the degradation of TCAA by electrochemical and sonoelectrochemical methods, as the main dechlorination mechanism is the sequential C-Cl bond cleavage,

which is enhanced by the physical and chemical effects produced by the presence of cavitation phenomena. For this purpose, commercially available materials such as stainless steel, carbon and Ti were evaluated as potential cathode materials for the sonoelectrochemical degradation of TCAA and its by-products, along with a less usual material such as Pb, which has already been successfully employed in the electroreduction of other chlorinated organocompounds [36].

2. Experimental

The same chemicals, analytical methods and experimental set-up previously used for the evaluation of the anode material on the sonoelectrochemical degradation of TCAA [35] were again used in the experiments included in the present study.

2.1. Chemicals and analytical methods

For all the experiments, 0.5 mM TCAA (99.9%, Aldrich) aqueous solutions were prepared with purified water (18.2 M Ω cm resistivity) from a Milli-Q UV Plus system. The concentration of TCAA and its main degradation by-products was monitored by analyzing 1 mL of sample filtered through a 0.45 μm PTFE filter with two different methods:

- High-performance liquid chromatography (HPLC) to monitor TCAA, DCAA MCAA and acetic acid (AA). An Agilent 1100 HPLC device fitted with a Hypersil ODS (C18) column (250 mm \times 4 mm and particle diameter 5 μm) and a UV-VIS detector set to a wavelength of 210 nm was used injecting 40 μL aliquots. The mobile phase was a phosphate buffer (pH 2.7) at 1 mL min⁻¹.
- Ionic chromatography (IC) to monitor TCAA, DCAA, MCAA and Cl⁻. A basic IC 792 System (Metrohm, Switzerland) equipped with a Metrosep A Supp 4/5 guard column, and an anion column Metrosep S Supp 9 μm (4.6 \times 250 mm) was used injecting 20 μL aliquots. The mobile phase was 1 mM Na_2CO_3 , 4 mM NaHCO_3 solution at 1 mL min⁻¹.
- Atomic absorbance spectroscopy (AAS) to monitor any traces of the metal cathodes in the treated water samples. A Perkin-Elmer 2100 equipped with an air-acetylene flame and an automatic simple injector AS-70 was used.

2.2. Experimental setup

All the reactions were carried out in a sonoreactor (0.5 L of volume) consisting of a cylindrical flask equipped with a cooling jacket where the electrodes (18 cm² on each side) were placed as shown in Fig. 1. The sonoreactor was assembled with an MFLG multifrequency system from Meinhardt Ultraschalltechnik, which operated at 863 kHz and 0.054 W cm⁻³ during the experiments with ultrasound. Electrochemical treatment (ECT) and sonoelectrochemical treatment (SECT) of prepared aqueous solutions were carried out for 10 h for each of the different cathode materials used. In all cases, the experiments were conducted at either a maximum current density of 4 mA/cm² or a maximum applied potential between cathode and anode of 14.3 V, depending of the different anode materials employed. In all the experiments, a homemade galvanostat (120 mA–13.4 V maxima power) was used. Four commercially available cathode materials were evaluated: Ti, AISI 304 stainless steel, carbon and Pb, all of them supplied by Goodfellow. Pt/Ti (50 g of platinum per m²) supplied by I.D. Electroquímica was used as the anode material in all the experiments as it was the anode where less anodic contributions to the overall degradation of TCAA and its main by-products were noticed in a previous work by the authors

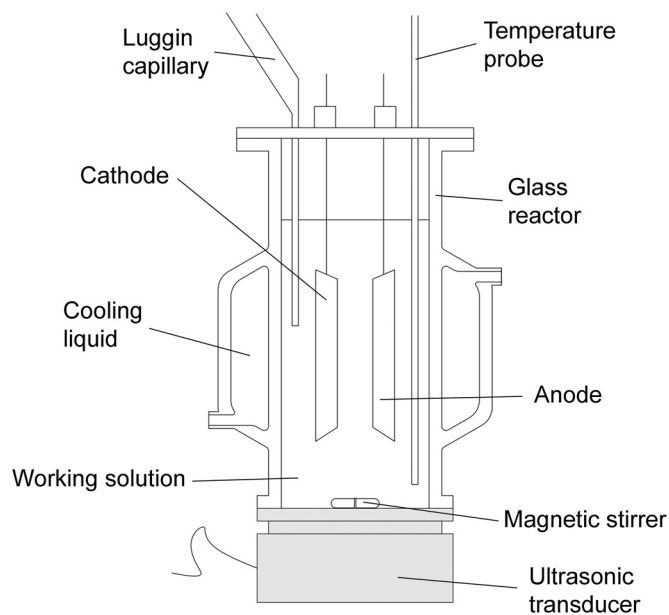


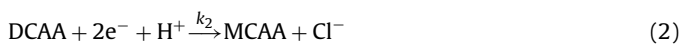
Fig. 1. Diagram showing the high-frequency sonoelectrochemical reactor used.

[35], the electrooxidation of the electrolyte being the main anodic process.

2.3. Kinetics

Two different dechlorination mechanisms were assumed in order to estimate the kinetics of the degradation of TCAA and its main by-products: (i) sequential C–Cl bond cleavage following the pathway of $\text{TCAA} \rightarrow \text{DCAA} \rightarrow \text{MCAA} \rightarrow \text{AA}$ [27–29,37] and (ii) the dissociative adsorption on the surface of the cathode which yields Cl^- ions and one-carbon fragments [37]. The sequential C–Cl bond cleavage and the dissociative adsorption would take place in the following stages:

Sequential C–Cl cleavage from TCAA to AA:



Degradation through dissociative adsorption:



where k_i ($i=1-6$) are the pseudo-kinetic constants in each reaction and X and Y represent the species needed in order to meet the principle of mass conservation. The study presented in this paper was focused on the analysis of the evolution of CAAs and Cl^- ions vs time (C–Cl bond cleavage was the main goal), and therefore, it was not necessary to determine such species. Reactions described by Eqs. (4)–(6) also take into account any cathodic and anodic phenomena leading to the mineralization of TCAA and its degradation by-products. It must be pointed out again that the anodic phenomena leading to the mineralization of TCAA and its degradation by-products should not have a significant influence in the present study due to the anode material, Pt/Ti, used in all the experiments.

First-order kinetics in a batch reactor were assumed, leading to the next set of equations for the mass balance of each of the species (TCAA, DCAA, MCAA, AA and chloride ions):

$$\frac{\partial[\text{TCAA}]}{\partial t} = r_{[\text{TCAA}]} = -k_1[\text{TCAA}] - k_4[\text{TCAA}] \quad (7)$$

$$\frac{\partial[\text{DCAA}]}{\partial t} = r_{[\text{DCAA}]} = k_1[\text{TCAA}] - k_2[\text{DCAA}] - k_5[\text{DCAA}] \quad (8)$$

$$\frac{\partial[\text{MCAA}]}{\partial t} = r_{[\text{MCAA}]} = k_2[\text{DCAA}] - k_3[\text{MCAA}] - k_6[\text{MCAA}] \quad (9)$$

$$\frac{\partial[\text{AA}]}{\partial t} = r_{[\text{AA}]} = k_3[\text{MCAA}] \quad (10)$$

$$\begin{aligned} \frac{\partial[\text{Cl}^-]}{\partial t} &= r_{[\text{Cl}^-]} \\ &= k_1[\text{TCAA}] + k_2[\text{DCAA}] + k_3[\text{MCAA}] + 3k_4[\text{TCAA}] \\ &\quad + 2k_5[\text{DCAA}] + k_6[\text{MCAA}] \end{aligned} \quad (11)$$

2.4. Figures of merit

The next process indicators were estimated in order to compare the ECT and SECT experiments conducted for the different cathode materials used in the present study:

1. Fractional conversion (FC):

$$\text{FC} = \frac{[\text{TCAA}]_{t=0} - [\text{TCAA}]_{t=t_f}}{[\text{TCAA}]_{t=0}} \times 100 \quad (12)$$

2. Degradation efficiency (DE):

$$\text{DE} = \frac{[\text{Cl}^-]_{t=t_f} - [\text{Cl}^-]_{t=0}}{3 \times [\text{TCAA}]_{t=0}} \times 100 \quad (13)$$

3. C mass balance error (C-MBE), where P indicates all the degradation compounds quantified:

$$\text{C-MBE} = \left(1 - \frac{\sum_{P=\text{compound}} (\text{mg of C in } P)_{t=t_f}}{(\text{mg of X in TCAA})_{t=0}} \right) \times 100 \quad (14)$$

4. Current efficiency (CE) regarding the dechlorination of TCAA and its chlorinated by-products, where V was the catholyte volume (L) and F was the Faraday constant (C mol^{-1}):

$$\text{CE} = \frac{[\text{Cl}^-]_{t=t_f} \times V \times 2 \times F}{\text{passed charge}} \times 100 \quad (15)$$

The synergic index (S_i) of the introduction of high-frequency ultrasound into the electrochemical degradation of TCAA was estimated for each cathode material according to the next expression [38]:

$$S_i = \frac{\text{DE}_{\text{SECT}}}{\text{DE}_{\text{ECT}} + \text{DE}_{\text{SCT}}} \quad (16)$$

where DE_{SECT} is the DE value estimated for SECT experiments, DE_{ECT} is the DE value estimated for ECT experiments and DE_{SCT} is the DE value for pure sonochemical treatment (SCT). Very low DE was achieved in the latter under similar ultrasonic conditions of frequency and power [35], being $\text{DE}_{\text{SCT}} \leq 2\%$.

3. Results and discussion

Fig. 2 displays the concentration of TCAA, DCAA, MCAA and AA, and Table 1 displays the figures of merit for ECT and SECT experiments performed with different cathode materials using a Pt/Ti

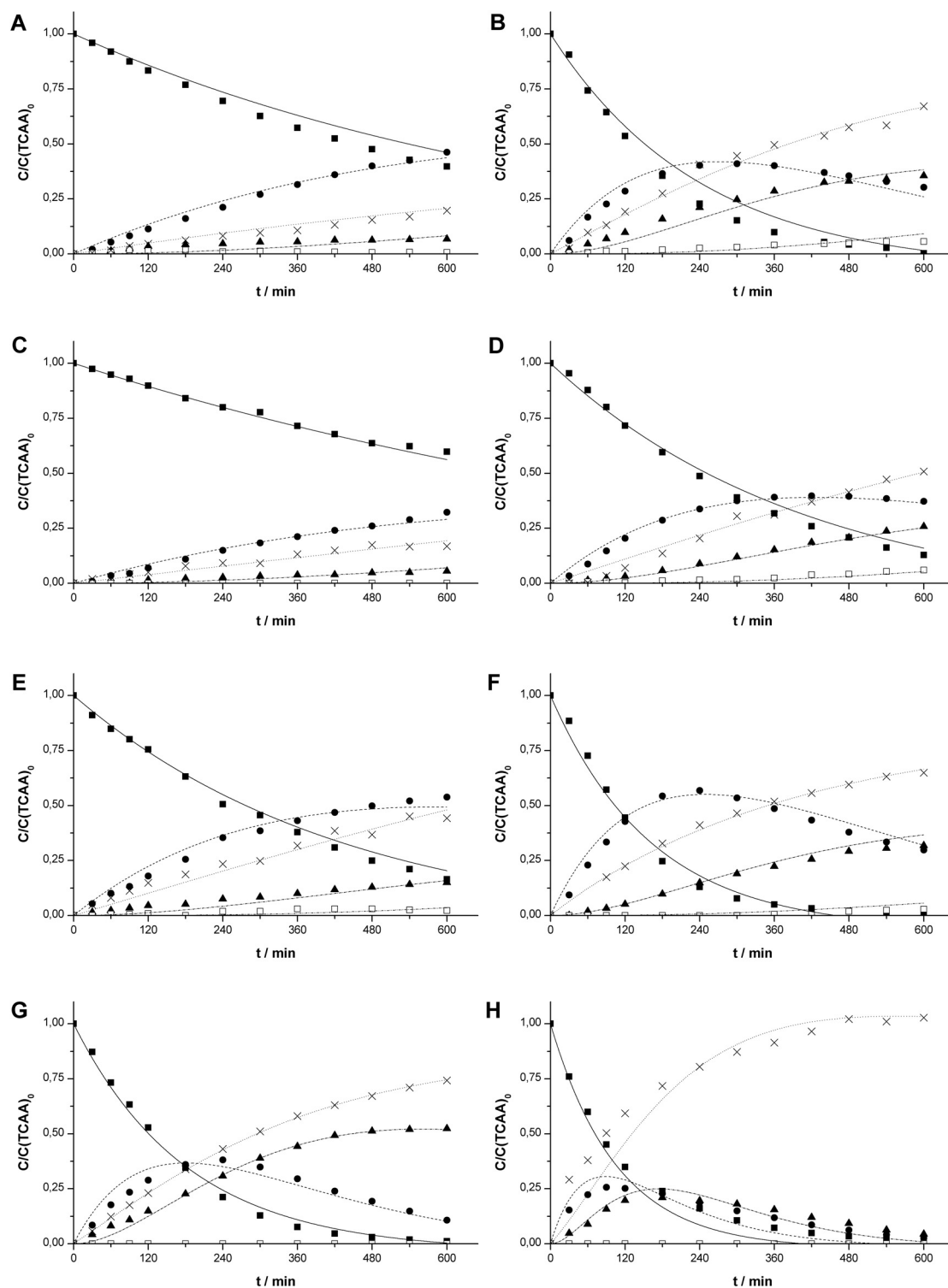


Fig. 2. Experimental normalized concentration of (■) TCAA, (●) DCAA, (▲) MCAA, (□) AA and (×) Cl^- , and the estimated normalized concentration of (—) TCAA, (---) DCAA, (----) MCAA, (-----) AA and (.....) Cl^- for ECT and SECT of 0.5 mM TCAA aqueous solution with different cathode materials: Ti (A: ECT, B: SECT), carbon (C: ECT, D: SECT), AISI 304 stainless steel (E: ECT, F: SECT) and Pb (G: ECT, H: SECT). Anode: Ti/Pt.

anode. When Ti, stainless steel and carbon cathodes were used, a remarkable increase in the decay of TCAA was observed when ultrasound was applied during the process, along with an increase in the formation and degradation rates of DCAA and MCAA, resulting in higher presence of Cl^- at the end of the process, which clearly indicates that the use of ultrasound catalyses the electrochemical dechlorination of TCAA. Moreover, for Ti and stainless steel

cathodes, a significant concentration of AA was obtained during the SECT experiments, whereas no formation of AA was noticed during the ECT experiments. The increase in the decay of TCAA was not as remarkable when using a Pb cathode under the presence of ultrasound as it was for the other cathode materials, as the Pb cathode already was reasonably effective in terms of the electroreduction of TCAA to DCAA. However, the evolution of the

Table 1
Estimated FC, DE, V_0 and S_i values for ECT and high-frequency SECT of 0.5 mM TCAA aqueous solution with different cathode materials and a Ti/Pt anode.

		Time (min)	FC (%)	DE (%)	$V_0 \times 10^5$ (mM s ⁻¹)	S_i
Ti	ECT	120	16.66	4.6	1.11 (R ² : 0.999)	2.5
		600	60.25	19.7		
	SECT	120	46.43	19.2	3.10 (R ² : 0.993)	
		600	99.80	55.2		
Carbon	ECT	120	10.13	4.9	0.67 (R ² : 0.997)	2.7
		600	40.16	16.8		
	SECT	120	28.34	7.0	1.88 (R ² : 0.990)	
		600	87.20	50.8		
AISI 304 stainless steel	ECT	120	24.53	14.8	1.63 (R ² : 0.978)	1.4
		600	83.61	44.1		
	SECT	120	55.56	22.5	3.97 (R ² : 0.997)	
		600	99.22	64.9		
Pb	ECT	120	47.22	23.0	3.18 (R ² : 0.997)	1.3
		600	98.85	74.3		
	SECT	120*	65.14	53.5	5.11 (R ² : 0.986)	
		600	98.49	96.9		

* This material-dependant effect is confirmed by the values of S_i , which are lower for all those materials (e.g. Pb and stainless steel) that showed better electro catalytical properties. Nevertheless, the fact that S_i was in all cases significantly higher than 1 clearly demonstrates the true synergistic nature of the combination of ultrasound and electrochemistry in the high-frequency sonoelectrochemical degradation of TCAA and its main degradation by-products.

concentration of DCAA and MCAA differed significantly in the presence of a high-frequency ultrasonic field, resulting in an almost complete degradation of TCAA, DCAA and MCAA with no formation of AA and very high concentrations of Cl⁻.

The different electrocatalytic properties of the cathode materials, and the catalytic effect that ultrasound has on the electrochemical degradation of TCAA and its main degradation by-products were not only observed in the increase of indicators such as FC, which is directly related to the concentration of TCAA in the treated solutions, but also in other indicators such as DE, CE and C-MBE. As the main objective of the study was to degrade the C–Cl bond, DE and CE were calculated considering the concentration of Cl⁻ in the water samples. For this reason, it was critical to account for all the chlorinated species present in the treated samples in order to make realistic conclusions regarding the sonoelectrochemical degradation of TCAA and its main degradation by-products, and in all the experiments included in the present study, Cl mass balance error was always lower than 5%. The catalysing effect of ultrasound in the total dechlorination of TCAA is remarkable when observing DE values (Table 1) for the ECT and SECT experiments conducted with each cathode, as DE was significantly higher for all the different cathode materials when using ultrasound, achieving a virtually complete

dechlorination when a Pb cathode was used. In addition, CE (Fig. 3) was generally higher in the presence of ultrasound than in silent conditions for all the cathode materials studied, although differences can be noticed in the evolution of EC during the degradation process depending on the cathode material. For Pb and carbon, a significantly higher CE is observed in the early stages of the experiments, although the current efficiency progressively decreases during the process, as the chemical species present in the water sample and its conductivity change during the process, resulting in an even higher electroreduction rate of the electrolyte, which is the main electrochemical reaction that occurs in the surface of the cathode.

The different cathode materials studied in the present study, with and without the presence of ultrasound, also behaved quite differently from the C-MBE point of view (Fig. 4). For the ECT experiments, the highest C-MBE values were always observed for the Pb cathode, whereas lower C-MBE values were reported for steel, Ti and carbon, in that respective order. This difference was even more significant in the presence of ultrasound, where very high C-MBE values were observed for the Pb cathode (C-MBE > 90% at $t = 600$ min) which may suggest the complete mineralization of TCAA, followed by steel, Ti and carbon. The initial rate of degradation of TCAA can also provide basic information on the catalytic

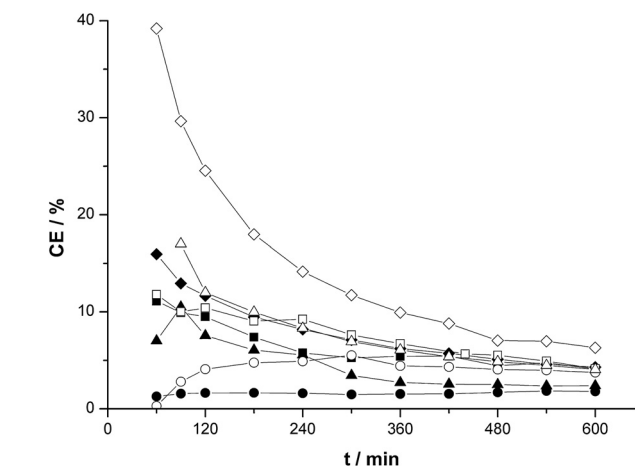


Fig. 3. Evolution vs time of the current efficiency (CE) for the ECT and high-frequency SECT of 0.5 mM TCAA aqueous solution with different cathode materials: Ti (■ ECT, □ SECT), carbon (● ECT, ○ SECT), AISI 304 stainless steel (▲ ECT, △ SECT) and Pb (◆ ECT, ◇ SECT). Anode: Ti/Pt.

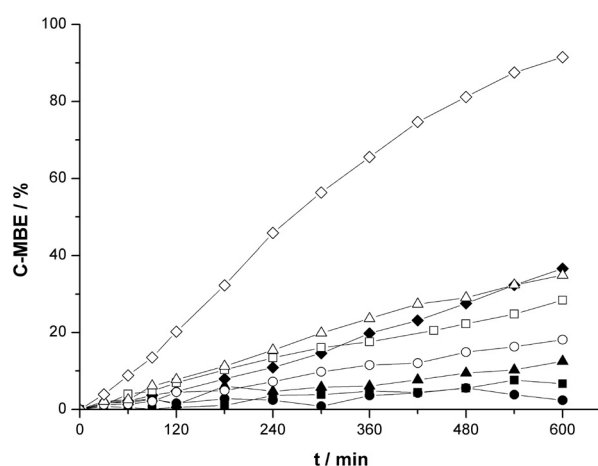


Fig. 4. Evolution vs time of the C mass balance error (C-MBE) for the ECT and high-frequency SECT of 0.5 mM TCAA aqueous solution with different cathode materials: Ti (■ ECT, □ SECT), carbon (● ECT, ○ SECT), AISI 304 stainless steel (▲ ECT, △ SECT) and Pb (◆ ECT, ◇ SECT). Anode: Ti/Pt.

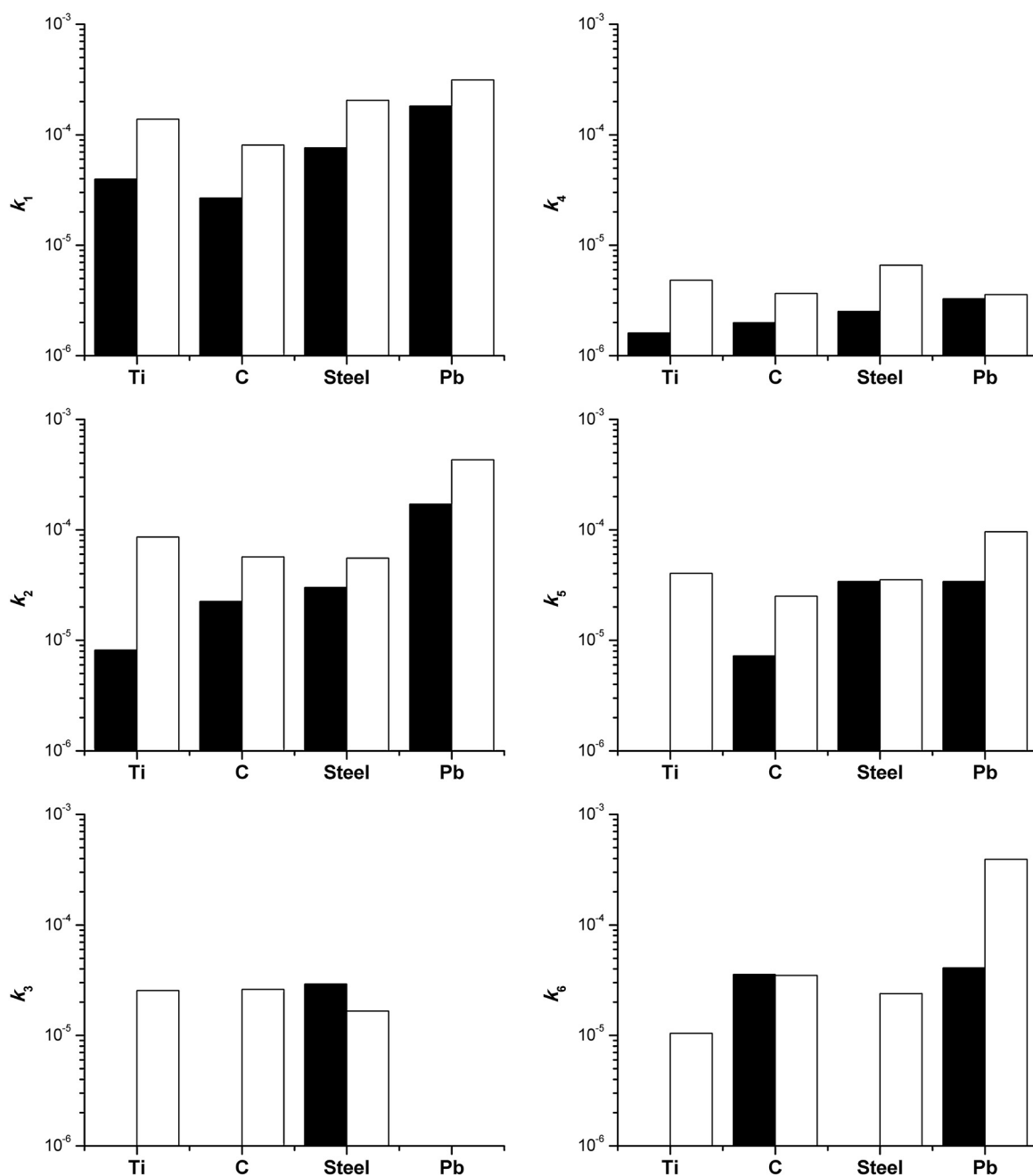


Fig. 5. First-order pseudo-kinetic constants estimated for the ECT and high-frequency SECT of 0.5 mM TCAA aqueous solution with different cathode materials (Ti, carbon, AISI 304 stainless steel and Pb) and a Ti/Pt anode.

effect that the introduction of high-frequency ultrasound has on the electrochemical dechlorination of TCAA with different cathode materials as the degradation process begins from the same initial conditions. Table 1 also shows the initial rate of degradation of TCAA estimated for the ECT and SECT experiments conducted with different cathode materials. A clear catalytic effect of the presence of high-frequency ultrasound is observed in all cases, as the introduction of ultrasound resulted in a significant increase in the initial degradation rate (V_0) for all the cathode materials. The effect is material-dependant: V_0 estimated during the ECT experiments for the cathode materials showing the worst electrocatalytic properties is almost tripled, while 'only' a 60% improvement is achieved in the case of Pb. This material-dependant effect is confirmed by the values of S_i , which are lower for all those materials (e.g. Pb and stainless steel) that showed better electro catalytic properties.

Nevertheless, the fact that S_i was in all cases significantly higher than 1 clearly demonstrates the true synergistic nature of the combination of ultrasound and electrochemistry in the high-frequency sonoelectrochemical degradation of TCAA and its main degradation by-products.

All these differences in terms of DE, CE and C-MBE are caused by the different dechlorination mechanisms that may take place on the surface of the cathode and how they are affected by the cathode material and the presence of ultrasound, as observed in Fig. 5, which compares the pseudo-kinetic constants estimated for ECT and SECT experiments conducted with the different cathode materials used in the study. For the Ti cathode, the electroreduction of TCAA in the absence of ultrasound (ECT) mainly occurs through the progressive C–Cl bond cleavage to MCAA, which is no longer degraded, while only a small amount of TCAA is degraded

via the dissociative adsorption route ($k_1 > k_2 > k_4$, $k_3 = k_5 = k_6 = 0$). The presence of ultrasound (SECT) not only significantly increased the values of k_1 , k_2 and k_4 , but also had a remarkable effect on the degradation mechanisms: while TCAA was still mainly reduced to DCAA, DCAA was now degraded by electroreduction to MCAA and by dissociative adsorption (k_2 and k_5 have the same order of magnitude), and MCAA is now not only reduced to AA (which was now detected in the SECT experiment), but also degraded via the dissociative adsorption route. In the case of carbon cathode, the dechlorination of TCAA in the absence of ultrasound mainly occurs through the progressive C–Cl bond cleavage ($k_1 > k_4$ and $k_2 > k_5$) down to the generation of MCAA, which is then degraded only via the dissociative adsorption mechanism ($k_3 = 0$). Again in this case, when ultrasound is introduced in the process (SECT), the progressive electroreduction of TCAA is catalysed to a point where AA is now detected, achieving a complete dechlorination via the C–Cl bond cleavage route. The dissociative adsorption route is also enhanced with ultrasound (k_4 and k_5 values are significantly higher for SECT compared with those same pseudo-kinetic constants estimated for ECT), although the final degradation of MCAA via the dissociative adsorption route is now slightly less effective (k_6 is slightly lower for SECT than for ECT) due to the fact that the electroreduction of MCAA to AA is achieved under the presence of ultrasound, gaining much more importance in terms of degradation of MCAA. For the steel cathode, some differences were observed in the absence of ultrasound (ECT): TCAA was again mainly electroreduced to DCAA ($k_1 > k_4$), whereas the formed DCAA was degraded through both electroreduction to MCAA and the dissociative adsorption route, being the latter more effective ($k_5 > k_2$). The formed MCAA was in this case completely degraded by electroreduction, forming AA. In the presence of ultrasound (SECT), besides the general improvement in both degradation mechanisms (higher values were estimated for k_{1-4}), less AA was detected during the experiments while a higher degree of degradation of MCAA was achieved, which suggests a catalytic effect of ultrasound on the dechlorination of MCAA via the dissociative adsorption mechanism to the point that the latter became even more efficient than the electroreduction from MCAA to AA route. Finally, we can comment on the case of the Pb cathode. In the absence of ultrasound (ECT), the progressive C–Cl bond cleavage ($k_1 > k_4$ and $k_2 > k_5$) down to the generation of MCAA proved very effective, whereas MCAA was only degraded via the dissociative adsorption mechanism ($k_3 = 0$). The Pb cathode was so effective due to its electrocatalytic properties that a higher DE was achieved with such cathode material in the absence of ultrasound (ECT) than with the other cathode materials in the presence of ultrasound (SECT). But again, as with the other cathode materials, the introduction of high-frequency ultrasound resulted in a further enhancement of the process to the point where complete dechlorination of TCAA was virtually achieved. In this case though, despite the enhancement observed in the overall efficiency of the SECT, no significant changes in the degradation mechanisms were observed, as MCAA was still degraded via the dissociative adsorption mechanism only.

The results obtained during the study did not only show the electrocatalytic properties of the different cathode materials, but also how these can be further enhanced by the presence of high-frequency ultrasound. Regarding this, the kinetics of the overall degradation were enhanced, showing how the overall degradation pathways and mechanisms varied with high-frequency ultrasound. This would be partly due to the different physical (e.g. micro-jetting and micro-mixing [30]) and chemical effects related to the presence of acoustic cavitation caused by a high-frequency ultrasonic field. Related to this, although the formation of acoustic cavitation on its own does not have a significant effect on the degradation of TCAA (very poor degradation of TCAA is achieved with pure sonochemical methods [35,39]), the chemical effect of the presence of cavitation

Table 2

Metal levels after high-frequency SECT of 0.5 mM TCAA aqueous solution with different cathode materials and a Ti/Pt anode and maximum permitted metal levels in drinking water (U.S. EPA).

	Material (ppm)	Maximum permitted according to U.S. EPA (ppm)
Ti	Not detected	N/A
Carbon	N/A (small particles suspended in solution)	N/A
AISI 304 stainless steel	0.1 (Fe)	0.3 (Fe)
Pb	2.1	0.015

phenomena near the surface of the electrodes in terms of electrode activation and formation of reaction intermediates in the electrodic reactions must not be discarded.

It is necessary, at this point, to comment on the stability of the cathode materials under the highly energetic conditions potentially achieved during the SECT experiments, which involve the presence of cavitation phenomena in the electrolyte. Erosion by ultrasonic cavitation is well known [40], although such phenomenon, which is mainly due to the mechanical effects resulting from the presence of ultrasonic cavitation, is far more significant at low frequencies [41]. Such erosion effect of ultrasound on the surface of the cathode could lead to the presence of suspended particles originated from the cathode, potentially resulting in an undesired level of hazardous materials (e.g. Pb) in the treated water. Table 2 shows the concentration of each cathode material measured in the treated water samples at the end of the SECT experiments and their maximum concentration established by both the U.S. EPA and the WHO organizations for drinking waters. When using Ti, carbon and steel as the cathode materials, the presence of such materials is significantly smaller than the required by the legislation, proving the suitability of the use of such materials for the sonoelectrochemical decontamination of drinking waters polluted with TCAA. However, the case of Pb is different, as the concentration of Pb observed in the treated solution after the SECT is significantly higher than the permitted limits. As Pb is the most promising cathode material among those tested in the present study, it is worth doing a more detailed discussion regarding the high levels of Pb found in the solutions treated with ultrasound (SECT), not only due to the hazardous nature of such material, but also due to the critical effect that dissolved/suspended Pb may have on the efficiency of the process. First of all, the reason why the water treated with the Pb cathode is by far the one with the highest content of cathode material after the SECT experiments must be identified. Cathode degradation could occur by chemical, physical or even electrochemical (i.e. corrosion) under the high-frequency conditions set during the SECT experiments. Assuming the erosion effect of ultrasound on the surface of the cathode, if the cathode materials were ordered in terms of its hardness in the Mohs scale (from lower to higher), we would see that 1 would be the hardness for carbon (graphite), 2.5 for Pb, 6 for Ti and 9 for steel (AISI 304), meaning that mechanical degradation by ultrasound is reasonable for the softest materials used such as Pb (for the carbon cathode, small suspended particles were observed in the solution). If we take a look at its Pourbaix diagram, Pb should be at a potential protected against corrosion [42], as the reduction of water and the consequent hydrogen evolution was observed during the experiment. Nevertheless, the small particles of Pb formed by the erosion effect of ultrasonic cavitation could react with TCAA and its degradation by-products. To confirm this, a small piece of Pb (1 g) was left for 200 h in a small sample of water (20 mL) containing a high concentration of TCAA (130 mM), and the resulting bulk solution was analysed to detect any degradation of TCAA. TCAA reacted with the Pb, yielding 66% of DCAA and 6% of MCAA (C-MBE < 5%) demonstrating that, as opposed to the other materials used (no changes in the concentration of TCAA and no presence of

DCAA and MCAA were detected in similar tests conducted with 1 g of Ti, carbon and steel), Pb is not an inert material when it is in contact with very high concentrations of TCAA, potentially leading to the reduction of TCAA to DCAA and MCAA. Going back to the SECT using a Pb cathode material, the small particles of Pb formed due to the erosion by ultrasonic cavitation could potentially react with TCAA present in the water and yield Pb^{2+} , which would be then electro-oxidised at the surface of the anode to PbO_2 , a process significantly catalysed under the presence of ultrasound [43]. In fact, the Pt/Ti anode used during the SECT conducted with the Pb cathode presented a much darker colour at the end of the experiment, possibly due to the electrodeposition of PbO_2 on the surface of the anode. The potential 'transformation' of the Pt/Ti anode into a PbO_2 anode would further enhance the degradation of CAAs via anodic mineralization, as suggested in previous studies [35]. In this sense, although the hazardous nature of Pb and the controversial use of this cathode for wastewater treatment is beyond doubt, it is also true that the electrodeposition of Pb is a very efficient process even at low concentrations, meaning that the potential removal of Pb by electrochemical methods, once the water polluted with TCAA and other CAAs has been treated, is a feasible option [44]. Discarding this cathode material due to the concentration levels included in Table 2 could therefore be a hasty decision.

4. Conclusions

The present study shows how the cathode material influences the electrochemical and high-frequency sonoelectrochemical degradation of TCAA and its main by-products, DCA and MCAA, in water samples where no background electrolyte was added (as in low-conductivity freshwaters). For all four cathode materials studied (Ti, AISI 304 stainless steel, carbon and Pb), the electrochemical degradation of TCAA was enhanced by the introduction of high-frequency ultrasound, not only due to the improvement of the progressive C–Cl bond cleavage mechanism, but also due to the enhancements of the dissociative adsorption/incineration mechanisms that may also take place. The best results were achieved when using a Pb cathode, where a virtually complete dechlorination of TCAA was achieved in presence of ultrasound.

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